APPENDIX D
CONSIDERATION OF TOTAL PETROLEUM HYDROCARBONS WITHIN THE DCRBCA PROCESS

LIST OF TABLES

APPENDIX D

CONSIDERATION OF TOTAL PETROLEUM HYDROCARBONS WITHIN THE DCRBCA PROCESS

D.1 INTRODUCTION

Petroleum products including gasoline, diesel, heating oils, etc. contain hundreds or even thousands of individual constituents with a range of physical, chemical, and toxicological properties. The properties of several of these chemicals are not known and it is not possible to calculate their risk-based target levels. Further it is impractical to analyze the concentration of each of these chemicals in the environmental media impacted by petroleum hydrocarbons. Thus a variety of approaches have been developed to estimate media-specific target levels and to identify the key constituents for the management of petroleum, specifically heating oil, diesel impacted sites. These approaches include:

1. Target levels for total petroleum hydrocarbon (TPH) concentration,
2. Target levels for specified ranges of petroleum hydrocarbons e.g. TPH-GRO, TPH-DRO, and TPH-ORO,
3. Target levels for a few constituents (those considered most toxic and for which sufficient data is available) e.g. benzene, toluene, ethylbenzene, xylenes, napthalene and PAHs,
4. Target levels for a specified size range of aromatic and aliphatic fractions, e.g. aliphatics >C6-C8, aliphatics C8-C10, aromatics C10 - C20, etc.,
5. A combination of the above approaches.

Each of the above approaches is approximate. However, in each case the field sampling and analysis approach should be consistent with the approach used to develop target levels. For example, if target levels are developed for specific aromatic and aliphatic fractions, (approach 4 above), soil and groundwater samples should be analyzed for the corresponding fractions. Note the laboratory analysis cost for measuring TPH concentration are significantly lower than for measuring individual fractions, thus the selection of a particular approach has significant cost implications. If cost were not an issue, measurement of individual fractions (Approach 4) would be the preferred approach.

Within the DCRBCA process, petroleum hydrocarbon impacts will be evaluated using the following approach:

- For Tier 1 and Tier 2A evaluations, develop target levels for the individual COCs identified in Table 4-1, and for TPH-GRO (gasoline range organics), TPH-DRO (diesel range organics), and TPH-ORO (oil range organics). Thus for the comparison of risk based levels with representative site concentrations, it will be necessary to analyze soil samples for the individual constituents as well as TPH-

GRO, TPH-DRO, and TPH-ORO using method 8015 (modified). This is a combination of Approach 2 and 3 above. If available, analytical data for TPH fractions may be used for Tier 1 and Tier 2A evaluations.

- For Tier 2B evaluations, either use the above approach or develop target levels for the COCs and specified petroleum fractions using the National TPH Criteria Working Group Method. This method is an enhancement of that used by Massachusetts Department of Environmental Protection (MDEP).

  The National TPH Criteria Working Group was based on a very exhaustive study of the petroleum products, their fate and transport properties, and toxicity. The National Criteria TPH Working Group was established in 1993 and consisted of over 400 participants from numerous organizations including USEPA, industry, consulting companies, and trade organizations. The goal of this group was to develop scientifically defensible information for establishing soil cleanup levels protective of human health and the environment. The efforts of this group culminated in the publication of four volumes (see reference list).

The remaining portion of this appendix describes the data used to develop Tier 1 screening levels for TPH-GRO, TPH-DRO, and TPH-ORO and individual petroleum fractions. The same method can be implemented using site-specific data to develop Tier 2A target levels.

D.2 DEVELOPMENT OF TIER 1 AND TIER 2A TARGET LEVELS.

As mentioned in Chapter 5 of this document, development of target levels requires the following information:

1. Target risk level for carcinogenic as well as non-carcinogenic adverse health effects. For specific discussion, refer to Section 5.3.1. Note currently these TPH fractions are evaluated for non-carcinogenic effects only.

2. Fraction-Specific Physical and Chemical properties. These are discussed in Section 5.3.2 and Section D.3 below for the specific fractions.

3. Quantitative toxicity values. These are discussed in Section 5.3.3 and in Section D.4 below for the specific fractions.

4. Receptor specific exposure factors. For specific discussion refer to Section 5.3.4.

5. Fate and transport parameters. For specific discussion refer to Section 5.3.5.

6. Intake equations and fate and transport models. For specific discussion refer to Section 5.3.6 and Appendix C.

Thus the overall approach for developing Tier 1 and Tier 2A screening levels for the petroleum fractions is the same as that described in Section 5.0, except for the chemical specific properties discussed below.

D.3 FRACTION-SPECIFIC PHYSICAL AND CHEMICAL PROPERTIES

Table D-1 lists the chemical-specific properties of the petroleum fractions used by several different entities, namely (TNRCC), Massachusetts Department of Environmental Protection (MDEP), and the National Criteria TPH Working Group. As mentioned above the TPH Working Group data were used in the DCRBCA process.

D.4 TOXICOLOGICAL PROPERTIES OF VARIOUS FRACTIONS

Table D-1 lists the toxicological properties of the petroleum fractions used by several entities. As mentioned above the TPH Working Group data was used in the DCRBCA process.

D.5 DEVELOPMENT OF TIER 1 AND TIER 2A TARGET LEVELS FOR TPH-GRO, TPH-DRO, AND TPH-ORO

Table D-2 lists the aromatic and aliphatic fractions included in each of the three TPH groups namely: TPH-GRO, TPH-DRO, and TPH-ORO. These fractions are consistent with the SW846 analytical method 8015 (modified).

Risk-based screening levels for TPH-GRO, TPH-DRO, and TPH-ORO were developed using the following steps:

Step 1: Calculate target levels for individual TPH fractions (Each TPH fraction is treated as an individual chemical and the computational software is set up to calculate target levels for each fraction.)

Step 2: If the value obtained for a fraction in Step 1 exceeded the theoretical maximum concentration (soil saturation for soil and solubility for groundwater), replace that value with the theoretical maximum value.

Step 3: Add the target level, from Step 2, for each fraction within a TPH group (see Table D-2 for a list of fractions within each group) to obtain the target level for that particular TPH group. (Some fractions may not have a target level for a particular pathway because that particular fraction does not have any toxicity data.)

Step 4: In Step 2, if the target levels for all the fractions within a particular TPH group exceeded the theoretical maximum concentration (soil saturation for soil and solubility for groundwater), the target level calculated in Step 3 for that particular group is assumed to exceed the theoretical maximum concentration.

The computational software is set up to perform these steps automatically and the TPH group target levels will be automatically generated and displayed. The calculated Tier 1 values are tabulated in the tables in Chapter 5 of this document.

D.6 SITE-SPECIFIC IMPLEMENTATION OF THIS APPROACH

- For the Tier 1 and Tier 2A implementation of the DCRBCA process, the responsible party should collect and analyze soil and groundwater concentration of the individual constituents as well as the three TPH groups using the methods indicated in Table 4-1. Since the measured value of TPH-GRO includes the contribution of BTEX concentration, it is necessary to subtract the total BTEX concentration from the measured TPH-GRO prior to comparing it with the Tier 1 and Tier 2A target levels. This correction to the measured TPH-GRO concentrations will ensure that the comparison of the measured and the target values is consistent with the assumptions used to estimate the tiered approach. If available, analytical data for TPH fractions may be used for Tier 1 and Tier 2A evaluations.

For a Tier 2B evaluation, the responsible party may use either the approach used for Tier 2A evaluation or use the TPH Working Group method to estimate the risk based levels for each of the TPH fractions. Note if the Working Group Method is used, the responsible party must collect soil and ground water data for these individual fractions to estimate representative concentrations.

REFERENCES

Texas Natural Resources Conservation Commission*; **Development of Human Health PCLs for Total Petroleum Hydrocarbon mixtures, June 2000.***

Total Petroleum Hydrocarbon Criteria Working Group*: **Volume 1; Analysis of Petroleum Hydrocarbons in Environmental Media, Amherst Scientific Publishers, 1997.***

Total Petroleum Hydrocarbon Criteria Working Group*: **Volume 2; Composition of Petroleum Mixtures, Amherst Scientific Publishers, 1997.***

Total Petroleum Hydrocarbon Criteria Working Group*: **Volume 3; Selection of representative TPH Fractions Based on Fate and Transport Considerations, Amherst Scientific Publishers, 1997.***

Total Petroleum Hydrocarbon Criteria Working Group*: **Volume 4; Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH, Amherst Scientific Publishers, 1997.***

Massachusetts Department of Environmental Protection; ***Characterizing Risks Posed by Petroleum Contaminated Sites – Implementation of MADEP VPH/EPH Approach, October 1997.***

TABLE D-1

TPH fractions ; physical chemical and toxicological properties used by indicated groups.

TEXAS NATURAL RESOURCES CONSERVATION COMMISION [A]										
Fraction	RfDo [mg/kg-day]	RfCi [mg/m^3]	RfDi [mg/kg-day]	MW [g/mole]	H [cm3-water/ cm3-air	Log Koc	Dair [cm2/s]	Dwater [cm2/s]	Solubility [mg/L]	Vapor Pressure [mm Hg]
Aliphatics										
C6	0.06	2.0E-01/1.8E+01m	0.057/5.143 m	81	33	2.9	0.1	1.00E-05	36	270
>C6-C8	0.06	2.0E-01/1.8E+01m	0.057/5.143 m	100	50	3.6	0.1	1.00E-05	5.4	48
>C8-C10	0.1	1	0.2857	130	80	4.5	0.1	1.00E-05	0.43	4.8
>C10-C12	0.1	1	0.2857	160	120	5.4	0.1	1.00E-05	0.034	0.48
>C12-C16	0.1	1	0.2857	200	520	6.7	0.1	1.00E-05	7.60E-04	0.036
>C16-C35*	2	---		270	4900	8.8	0.1	1.00E-05	2.50E-06	8.40E-04
Aromatics										
>C7-C8	0.1	0.4	0.1143	92	0.276	2.15	0.087	8.60E-06	530	28.2
>C8-C10	0.04	0.2	0.0571	120	0.48	3.2	0.1	1.00E-05	65	4.8
>C10-C12	0.04	0.2	0.0571	130	0.14	3.4	0.1	1.00E-05	25	0.48
>C12-C16	0.04	0.2	0.0571	150	0.053	3.7	0.1	1.00E-05	5.8	0.036

>C16-C21	0.03	---		190	0.013	4.2	0.1	1.00E-05	0.65	8.40E-04
>C21-C35*	0.03	---		240	6.70E-04	5.1	1	1.00E-05	6.60E-03	3.30E-07

*Analysis may be truncated at C28 if there does not appear to be significant amounts of higher carbons

m: For mixtures with less than 53% n-hexane content

For the toxicity data, surrogate chemicals were used to obtain values

TOTAL PETROLEUM HYDROCARBON CRITERIA WORKING GROUP										
Fraction	RfDo [mg/kg-day]	RfCi [mg/m^3]	RfDi [mg/kg-day]	MW [g/mole]	H [cm3-water/ cm3-air	Log Koc	Dair [cm2/s]	Dwater [cm2/s]	Solubility [mg/L]	Vapor Pressure [atm]
Aliphatics										
>C6-C8	5	5.3	1.5143	100	50	3.6	NA	NA	5.4	0.063
>C8-C10	0.1	0.3	0.0857	130	80	4.5	NA	NA	0.43	6.30E-03
>C10-C12	0.1	0.3	0.0857	160	120	5.4	NA	NA	0.034	6.30E-04
>C12-C16	0.1	3	0.8571	200	520	6.7	NA	NA	7.60E-04	4.80E-05
>C16-C35	2	NA		270	4900	8.8	NA	NA	1.30E-06	1.10E-06
Aromatics										
>C8-C10	0.04	0.2	0.0571	120	0.48	3.2	NA	NA	65	6.30E-03
>C10-C12	0.04	0.2	0.0571	130	0.14	3.4	NA	NA	25	6.30E-04
>C12-C16	0.04	0.2	0.0571	150	0.053	3.7	NA	NA	5.8	4.80E-05

>C16-C21	0.03	NA		190	0.013	4.2	NA	NA	0.65	1.10E-06
>C21-C35	0.03	NA		240	6.70E-04	5.1	NA	NA	6.60E-03	4.40E-10

MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION										
Fraction	RfDo [mg/kg-day]	RfCi [mg/m^3]	RfDi [mg/kg-day]	MW [g/mole]	H [cm3-water/ cm3-air	Koc	Dair [cm2/s]	Dwater [cm2/s]	Solubility [mg/L]	Vapor Pressure [atm]
Aliphatics										
>C5-C8	0.06	200	57.143	93	54	2265	0.08		11	0.1
>C9-C12	0.6	2000	571.429	149	65	157.5	0.07		0.07	8.70E-04
>C9-C18	0.6	2000	571.429	170	69	714	0.07		0.01	1.40E-04
>C19-C36	6	NA		Considered immobile						
Aromatics										
>C9-C10	0.03	60	17.143	120	0.33	1778	0.07		51	2.90E-03
>C11-C22	0.03	71	20.286	150	0.03	5000	0.06		5.8	3.20E-05

References:
A - TNRCC; Development of human health PCLs for Total Petroleum Hydrocarbons Mixtures, June 2000

NA: Not Available

Table D-2
Constituent fractions of TPH groups

TPH GROUP	TPH FRACTIONS USED
TPH-GRO (C6-C10)	Aliphatics >C6-C8 >C8-C10 Aromatics >C8-C10
TPH-DRO (C10-C24)	Aliphatics >C10-C12 >C12-C16 >C16-C35 Aromatics >C10-C12 >C12-C16 >C16-C21
TPH-ORO (C24+)	Aromatics >C21-C35